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A NON-PERMSELECTIVE MEMBRANE REACTOR FOR CHEMICAL PROCESSES NORMALLY REQUIRING STRICT STOICHIOMETRIC FEED RATES OF REACTANTS

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ABSTRACT

A novel type of membrane reactor with separated feeding of the reactants is presented for chemical processes normally requiring strict stoichiometric feed rates of premixed reactants. The reactants are fed in the reactor to the different sides of a porous membrane which is impregnated with a catalyst for a heterogeneously catalyzed reaction. If the reaction rate is fast compared to the diffusion rates of the reactants, a small reaction zone inside the membrane occurs and slip of one of the reactants to the opposing side of the membrane is prevented. The location of this reaction zone will be such that the molar fluxes of the reactants are always in stoichiometric ratio. The features of this reactor are shown by means of mathematical modelling of molecular diffusion and viscous flow combined with an instantaneous, reversible reaction inside the membrane. As a model reaction the Claus reaction was selected and by conversion measurements the principle of a shifting reaction plane inside a porous membrane is demonstrated.

KEY WORDS

Membrane reactor, ceramic membranes, Claus reaction, modelling, desulfurization.

INTRODUCTION

Considerable research effort has recently been devoted to membrane reactors. The studies involving membrane reactors presented in literature can be divided in two classes; biological systems and systems where the membrane is used to shift the equilibrium of a reversible reaction (Mohand and Govind, 1988). In the present investigation, a new type of membrane reactor is presented in which the reaction takes place inside the catalytically active membrane and, contrary to usual applications, the permselectivity of the membrane is not important. In Fig. 1 a schematic representation of this membrane reactor is given.

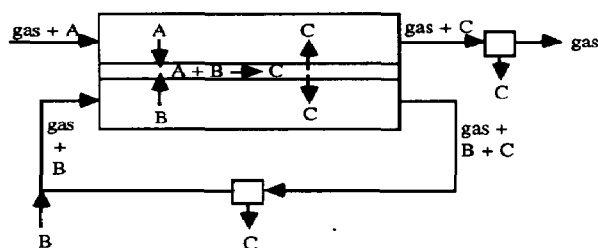
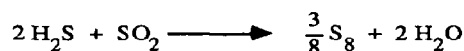


Fig. 1: Schematic representation of the membrane reactor.

The reactants are fed to the different sides of a porous membrane which is impregnated with a catalyst for a heterogeneous chemical reaction. Inside the membrane the reaction takes place. The products diffuse out of the membrane to both sides. If the rate of the reaction is fast compared to the diffusion rates of the reactants in the membrane, a small reaction zone will be present in the membrane, ultimately leading to a reaction plane for instantaneous, irreversible reactions. At this reaction zone/plane the molar fractions of both reactants will be very low. The molar fluxes of the reactants are, in absence of a pressure difference over the membrane, determined by their driving forces, their diffusion coefficients and the distance to the reaction zone. If for some reason these molar fluxes are temporary not in stoichiometric ratio, there will be an excess of one of the reactants at the reaction zone which will penetrate deeper into the membrane to react with the other reactant. As a result, the location of the reaction zone shifts toward the side of the reactant with the molar flux below stoichiometry. As the distance to the reaction zone decreases for the last mentioned reactant its molar flux increases and the molar flux of the other reactant decreases. Finally, the location of the reaction zone/plane will be such that the molar fluxes of the reactants are always in stoichiometric ratio and slip of one of the reactants to the opposing side of the membrane is prevented. The membrane reactor operated as described above can therefore be regarded as a very suitable reactor for processes normally requiring strict stoichiometric feed rates of reactants.

In this work the Claus reaction (Mark H.F. *et al.*, 1983) has been selected as a model reaction to study the proposed membrane reactor.



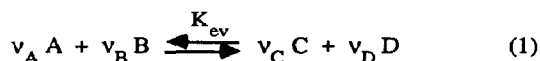
The membrane used was made of $\alpha\text{-Al}_2\text{O}_3$ with a mean porediameter of 350 nm, impregnated with $\gamma\text{-Al}_2\text{O}_3$, the catalyst for the Claus reaction. The Claus reaction however, cannot be regarded as irreversible but is actually an equilibrium reaction instead and therefore the influence of reversibility on the reactor performance has to be determined. Another effect that may have a pronounced effect on the reactor performance is the occurrence of a pressure difference over the membrane. In order to study both the influence of reversibility and a pressure difference, a mathematical model has been developed which describes the transport and reaction in this membrane reactor. In the model, the transport of reactants and products takes place by simultaneous viscous flow and molecular diffusion while the reaction is assumed to be instantaneous and reversible.

MODEL DESCRIPTION

The model developed in the present study is a flux model

reflecting the experimental set up used to study the Claus reaction in the membrane reactor consisted of two well mixed chambers. For simulation of a practical application of the membrane reactor, this flux model has to be incorporated into a reactor model which takes the operation mode (co- or countercurrent) into account.

The instantaneous, reversible reaction can be presented generally by equation (1):



In the mathematical model mass transfer is described into one dimension, the direction perpendicular to the membrane and for steady state conditions. The model has to calculate the molar fractions of the reactants and products, x_A , x_B , x_C , x_D and, if present, of the inert component x_{inert} , and the pressure P as a function of the position in the membrane. As there are six variables to be determined six equations are required to describe mass transfer accompanied by a reversible, instantaneous reaction in the membrane.

The mass balance for component i in the stationary state is given by equation (2); the change of the molar flux of component i with the position in the membrane must be equal to the reaction rate at that position.

$$\frac{dJ_i}{dx} = R_i(x) \quad (2)$$

with $R_i < 0$ for reactants
and $R_i > 0$ for products

The mass balances for all components are presented by equations (3-7).

$$\frac{dJ_A}{dx} = R_A \quad (3)$$

$$\frac{dJ_B}{dx} = R_B = \frac{v_B}{v_A} R_A \quad (4)$$

$$\frac{dJ_C}{dx} = R_C = -\frac{v_C}{v_A} R_A \quad (5)$$

$$\frac{dJ_D}{dx} = R_D = -\frac{v_D}{v_A} R_A \quad (6)$$

$$\frac{dJ_{inert}}{dx} = 0 \quad (7)$$

As reaction (1) is regarded as an instantaneous equilibrium reaction compared to mass transfer, R_A is indefinite. Therefore R_A is eliminated by means of adding and subtracting among the equations (3-7) resulting in four independent equations (8-11):

$$\frac{1}{v_A} \frac{dJ_A}{dx} - \frac{1}{v_B} \frac{dJ_B}{dx} = 0 \quad (8)$$

$$\frac{1}{v_A} \frac{dJ_A}{dx} + \frac{1}{v_C} \frac{dJ_C}{dx} = 0 \quad (9)$$

$$\frac{1}{v_A} \frac{dJ_A}{dx} + \frac{1}{v_D} \frac{dJ_D}{dx} = 0 \quad (10)$$

$$\frac{dJ_{inert}}{dx} = 0 \quad (11)$$

In order to solve this set of equations uniquely two additional relations are required. The equilibrium condition is the fifth equation and is assumed to be valid through the entire membrane:

$$K_{ev} = \frac{x_C^{v_C} x_D^{v_D}}{x_A^{v_A} x_B^{v_B}} P^{-v_A - v_B + v_C + v_D} \quad (12)$$

The sum of the molar fractions must be equal to one which is the sixth and final equation:

$$\sum_{i=1}^{i=nc} x_i = 1 \quad (13)$$

Before the set of equations (8-13) can be solved, the molar flux of each component has to be specified. In the present study it is assumed that there are two mechanisms of transport, viscous flow and molecular diffusion according to Fick's law. These mechanisms are additive owing to the fact that they are independent.

$$J_i = x_i J_{visc} + J_{i,dif} \quad (14)$$

$$\text{with } J_{visc} = -\frac{1}{RT} \left(D_{inert,K} + \frac{B_0 P}{\eta} \right) \frac{dP}{dx} \quad (15)$$

$$\text{and } J_{i,dif} = -D_{i,eff} \frac{1}{RT} \frac{d(x_i P)}{dx} \quad (16)$$

The occurrence of the pressure in the driving force in equation (16) is necessary to take pressure diffusion into account (Mason and Malinauskas, 1983). The viscous flow is represented by the equation for the flow of a compressible fluid through a porous medium. The parameter B_0 is a membrane specific parameter defined according to equation (17).

$$B_0 = \frac{\varepsilon}{\tau} \frac{d_p^2}{32} \quad (17)$$

with ε the porosity, τ the tortuosity and d_p the mean pore diameter of the membrane

The effective diffusion coefficients $D_{i,eff}$ in the membrane are calculated according to resistances in series as given by equation (18).

$$D_{i,eff} = \frac{1}{\frac{1}{\varepsilon D_{i,K}^0} + \frac{1}{\varepsilon D_{i,inert}^0}} \quad (18)$$

The gaseous diffusion coefficients $D_{i,K}^0$ and $D_{i,inert}^0$ are estimated from gas kinetic theory (Reid *et al.*, 1977).

To solve the set of equations (8-18), twelve boundary conditions are required. At the membrane interfaces the equilibrium condition must be fulfilled (see equation (12)). Also the sum of the molar fractions must be equal to one at the interfaces (see equation (13)). The pressure at the membrane interfaces must be the same as the pressure in the bulk of the gas at that side of the membrane. The additional six boundary conditions required are obtained from mass balances coupling the molar fluxes from the bulk of the gas to the membrane interface, $J_{i,b-i}$, with the molar fluxes at the interface, $J_{i,int}$. Owing to the fact that the reaction is assumed to be instantaneous the molar fluxes from the bulk of the gas to the membrane interface, $J_{i,b-i}$, and the molar fluxes inside the membrane at the interface, $J_{i,int}$, do not have to be equal to each other but are coupled by the stoichiometry of the reaction (see equations (19a-19d)).

$$\frac{1}{v_B} (J_{B,b-i} - J_{B,int}) - \frac{1}{v_A} (J_{A,b-i} - J_{A,int}) = 0 \quad (19a)$$

$$\frac{1}{v_C} (J_{C,b-i} - J_{C,int}) + \frac{1}{v_A} (J_{A,b-i} - J_{A,int}) = 0 \quad (19b)$$

$$\frac{1}{v_D} (J_{D,b-i} - J_{D,int}) + \frac{1}{v_A} (J_{A,b-i} - J_{A,int}) = 0 \quad (19c)$$

$$J_{inert,b-i} = J_{inert,int} \quad (19d)$$

both at $x=0$ and $x=L$

There are eight mass balances at the membrane interfaces, however only six boundary conditions are required and therefore two mass balances must be left out. Equations (19d) are dropped as boundary conditions, however they will be necessary later on.

The molar fluxes inside the membrane at the interface $J_{i,int}$ in equations (19) are calculated by equations (14-16). The molar flux of component i from the bulk of the gas to the membrane interface $J_{i,b-i}$ consists of a viscous part and a diffusive part, see equation (20).

$$J_{i,b-i} = x_{i,b} J_{visc} - D_{i,inert}^0 \frac{P_{bulk}}{RT} \frac{dx_i}{dx} \bigg|_{b-i} \quad (20)$$

In equation (20) $b-i$ stands for $x = -\delta$ or $x = L + \delta$ for the two interfaces of the gas bulk with the gas film. The viscous molar flux in equation (20) J_{visc} is the same flux as inside the membrane and is given by equation (16) and is almost the same as the molar flux of inert. In fact equations (19d) that had to be dropped previously are used at this point. The derivative of the molar fraction at the interface of the gas bulk with the gas film in which the mass transfer resistance in the gas phase is situated, $(dx_i/dx)_{b-i}$ is however still unknown. This variable is determined by integration of the mass balance of component i in the gas film given in equation (21).

$$\frac{D_i P}{RT} \frac{d^2 x_i}{dx^2} - J_{visc} \frac{dx_i}{dx} = 0 \quad (21)$$

for $-\delta < x < 0$ and for $L < x < L + \delta$

The molar fractions x_i in the gas bulk, $x_{i,bulk}$, and at the membrane interface, $x_{i,int}$ where int stands for $x = 0$ or $x = L$, are used as boundary conditions to solve equation (21). The derivative of the molar fraction at the interface of the gas bulk with the gas film $(dx_i/dx)_{b-i}$, required in equation (20), is represented by equation (22).

$$\frac{dx_i}{dx} \bigg|_{b-i} = (x_{i,int} - x_{i,bulk}) * \frac{J_{visc}}{D_i^0} * \frac{RT}{P_{bulk}} * \frac{1}{\exp\left(\frac{J_{visc} RT \delta}{D_i^0 P_{bulk}}\right) - 1}$$

with δ the thickness of the stagnant gas film (22)

At $x=0$, the membrane interface at the side where A is fed to the reactor, and at $x=L$, the membrane interface at the B side, equations (19) are applied. Boundary conditions at both sides of the membrane required to solve the set of equations are the molar fractions of all components and the pressure in the bulk of the gas at both sides.

The mass transfer model consisting of this set of equations can only be solved numerically. The method used is a relaxation technique (Press *et al.*, 1986). In the relaxation method the set of N coupled differential equations is replaced by a set of N finite difference equations on a grid consisting of M mesh points. The discretization scheme is given in equations (23).

$$\frac{dx_i}{dx} = \frac{x_{i,k+1} - x_{i,k-1}}{2h} \quad (23a)$$

$$\frac{d^2 x_i}{dx^2} = \frac{x_{i,k+1} - 2x_{i,k} + x_{i,k-1}}{h^2} \quad (23b)$$

The first and second derivative of the pressure to the location in the membrane are also discretized according to equations (23). A solution of the set of equations to be solved consists of values for the N dependent variables at each of the M meshpoints, therefore a total number of $N*M$ variables. The method produces a matrix equation of size $N*M$ as presented in equation (24).

$$\begin{bmatrix} \frac{\partial E_{1,k=1}}{\partial v_{1,k=1}} & \dots & \frac{\partial E_{1,k=1}}{\partial v_{N,k=M}} \\ \vdots & & \vdots \\ \frac{\partial E_{N,k=M}}{\partial v_{1,k=1}} & \dots & \frac{\partial E_{N,k=M}}{\partial v_{N,k=M}} \end{bmatrix} * \begin{bmatrix} dv_{1,k=1} \\ \vdots \\ dv_{N,k=1} \\ \vdots \\ dv_{1,k=2} \\ \vdots \\ dv_{N,k=M} \end{bmatrix} = \begin{bmatrix} dE_{1,k=1} \\ \vdots \\ dE_{N,k=1} \\ \vdots \\ dE_{1,k=2} \\ \vdots \\ dE_{N,k=M} \end{bmatrix}$$

with E_{ij} the deviation of equation number i on grid point number j

$dv_{ij} = v_{ij,old} - v_{ij,new}$ where $v_{ij,old}$ is the present value of variable v_i at $k=j$

$$dE_{ij} = E_{ij,old} - E_{ij,new} = E_{ij,old} \quad (24)$$

Owing to the fact that the discretization of the derivatives of a variable $v_{i,k}$ only involves its values at the gridpoints $k-1$, k and $k+1$ the matrix with the partial derivatives consists of 3 grid points times 6 equations on each grid point so 18 diagonals in all. Solving equation (24) by inverting the matrix with partial derivatives gives new values of all variables simultaneously. By continuously improving the initial guessed solution the method is said to relax to the true solution (Press *et al.*, 1986).

NUMERICAL RESULTS:

Two sets of simulations were performed in order to study the influence of reversibility and of a pressure difference over the membrane. As base case, a simulation at a temperature of 200 °C in the absence of a pressure difference over the membrane was carried out. Owing to the fact that one of the products of the Claus reaction, elemental sulfur, has a melting point of about 119 °C, a temperature of at least 200 °C is required in order to be able to remove this product out of the membrane by diffusion through the gas phase. Parameters used in the simulation of the base case are given in Table 1, the molar fluxes calculated in Table 2.

Table 1: Parameters used in Fig. 2, 3 and 4.

bulk conditions

	H ₂ S side	SO ₂ side
$x_{\text{H}_2\text{S}}$	$1 * 10^{-2}$	$1 * 10^{-10}$
x_{SO_2}	$1 * 10^{-10}$	$1 * 10^{-2}$
x_{S_8}	$1 * 10^{-5}$	$1 * 10^{-5}$
$x_{\text{H}_2\text{O}}$	$1 * 10^{-2}$	$1 * 10^{-2}$
P (bara)	1.0 (Fig. 2 and 3) 1.5 (Fig. 4)	1.0

hydrodynamic parameter

$$k_g = \frac{D_{i, \text{inert}}^0}{\delta} = 1 * 10^{-2} \text{ m/s}$$

membrane parameters

$$B_o = 3 * 10^{-15} \text{ m}^2 \text{ (} d_p \approx 1 \mu\text{m)}$$

$$\varepsilon = 0.10$$

$$\tau$$

membrane thickness 3 mm

Equilibrium constant (Gamson and Elkins, 1953)

$$K_{\text{ev}} = \frac{x_{\text{S}_8}^{3/8} x_{\text{H}_2\text{O}}^2}{x_{\text{H}_2\text{S}}^2 x_{\text{SO}_2}} = 0.924 * 10^{-6} * \exp(1.274 * 10^4 / T) * P^{5/8}$$

with P in bar

Table 2: Molar fluxes calculated for Fig. 2 and 3.

	T = 200 °C		T = 300 °C	
	H ₂ S side	SO ₂ side	H ₂ S side	SO ₂ side
$J_{\text{H}_2\text{S}}$	$5.68 * 10^{-4}$	$4.38 * 10^{-6}$	$5.70 * 10^{-4}$	$4.31 * 10^{-5}$
J_{SO_2}	$-8.61 * 10^{-8}$	$-2.82 * 10^{-4}$	$-1.15 * 10^{-5}$	$-2.75 * 10^{-4}$
J_{S_8}	$-6.68 * 10^{-5}$	$3.89 * 10^{-5}$	$-6.68 * 10^{-5}$	$3.20 * 10^{-5}$
$J_{\text{H}_2\text{O}}$	$-3.44 * 10^{-4}$	$2.20 * 10^{-4}$	$-3.33 * 10^{-4}$	$1.94 * 10^{-4}$
J_{inert}	$1.99 * 10^{-5}$	$1.99 * 10^{-5}$	$2.86 * 10^{-5}$	$2.86 * 10^{-5}$

In Fig. 2 the calculated molar fraction profiles of this simulation are presented.

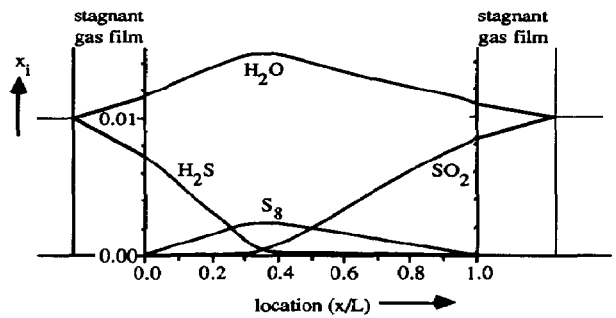


Fig. 2: Molar fraction profiles at 200 °C in absence of a pressure difference over the membrane

In Fig. 2 it can be seen that there is a considerable decrease of the molar fraction of H₂S and SO₂ from the bulk of the gas to the membrane interface and therefore mass transfer resistances in the gas phase are significant and cannot be neglected. As the reaction zone is very small in Fig. 2, the Claus reaction can be considered as almost irreversible at these conditions. From Table 2 it can be calculated that the slip of the reactants to the opposing side is less than 1 % of the molar flux of the reactants into the membrane.

The influence of reversibility was investigated by means of a simulation, carried out at a temperature of 300 °C also in the absence of a pressure difference over the membrane. Parameters used in this simulation are similar to the base case and are given in Table 1. The calculated molar fraction profiles are presented in Fig. 3.

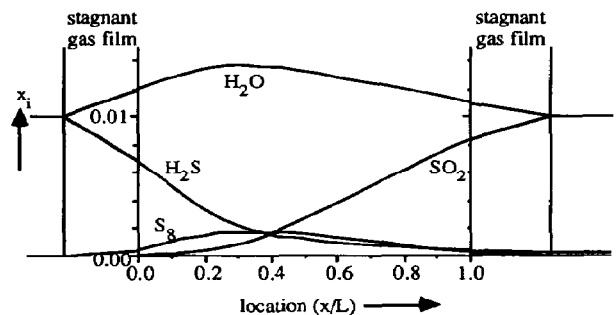


Fig. 3: Molar fraction profiles at 300 °C in absence of a pressure difference over the membrane

Molar fluxes calculated are given in Table 2. In Fig. 3 it can be seen that at 300 °C a broad reaction zone exists compared to the situation at 200 °C owing to the fact that the value of the equilibrium constant of the Claus reaction is much lower and therefore reversibility becomes more important. The effect of reversibility is also reflected by the slip of H₂S which is 8 % of the H₂S molar flux into the membrane as can be calculated from Table 2, compared to less than 1 % in the simulation at 200 °C. Comparing the conversion rates of H₂S, the molar flux of H₂S into the membrane minus the slip of H₂S, at 300 °C and at 200 °C it can be calculated from Table 2 that the conversion rate at 300 °C is only 6.5 % smaller than at 200 °C. So despite the fact that reversibility affects the molar fraction profiles and the slip of reactant substantially, the conversion rates of the reactants are hardly influenced.

In order to study the influence of a pressure difference over the membrane a simulation was carried out at a temperature of 200 °C and a pressure difference over the membrane of 0.5 bar with the highest pressure at the H₂S side. The molar fraction profiles are presented in Fig. 4.

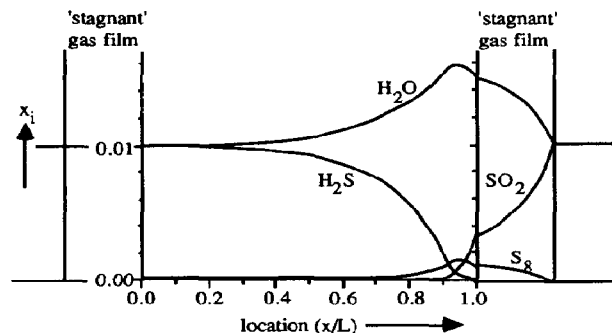


Fig. 4: Molar fraction profiles at 200 °C in the presence of a pressure difference of 0.5 bar

Parameters used are the same as in the base case, and are given in Table 1. In Fig. 4 it can be seen that owing to the pressure difference over the membrane, the reaction zone is shifted towards the low pressure side, the profiles become curved and the molar fraction of the low pressure side reactant SO₂ at the membrane interface drops compared to the situation without pressure difference. The curvature of the molar fraction profiles can be attributed to the fact that two transport mechanisms occur, viscous flow and molecular diffusion. As all H₂S reacts at the reaction zone, the total H₂S molar flux left of the reaction zone is constant. The H₂S flux consists of a viscous contribution and a diffusive contribution, which have a linear dependence on the molar fraction of H₂S and on the molar fraction gradient of H₂S respectively. As the molar fraction of H₂S decreases from the interface to the reaction zone, the viscous contribution decreases. To maintain a constant total molar flux of H₂S, the diffusive contribution must increase, resulting in an increase of the absolute value of the molar fraction gradient of H₂S leading to curved profiles. Owing to the fact that the presence of a viscous flow through the membrane from the H₂S side to the SO₂ side facilitates H₂S transport and reduces SO₂ transport, resulting in a decrease of the interface molar fraction of SO₂, the reaction zone is shifted toward the low pressure side in order to maintain stoichiometry between the H₂S and SO₂ molar fluxes. From these calculations, with parameters as given in Table 1, it can be concluded that despite the pressure difference of 0.5 bar over the membrane with a mean pore diameter of 1 μm, the reaction zone remains in the membrane and therefore the performance of the membrane reactor is not affected.

The quantitative effect of a pressure difference over the membrane on the molar fluxes was also investigated and therefore simulations were carried out at a temperature of 200 °C for various pressure differences. In Fig. 5 the molar flux of H₂S into the membrane at 200 °C is presented as a function of the pressure difference over the membrane.

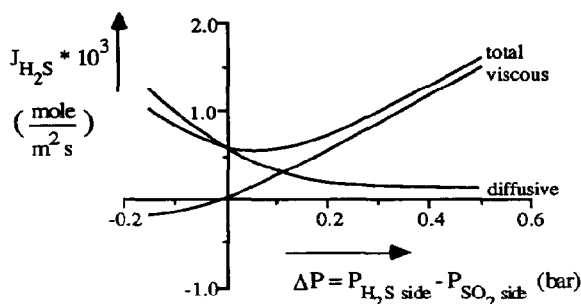


Fig. 5: Molar flux of H₂S into the membrane as a function of the pressure difference

Parameters used are given in Table 1. In this figure besides the total molar flux of H₂S into the membrane also its different contributions, viscous and diffusive, are given. Fig. 5 shows a minimum for the total molar flux of H₂S into the membrane. The occurrence of this minimum can be understood if the following asymptotic situations are considered. In case of a much higher pressure on the H₂S side, the H₂S molar flux is mainly determined by viscous flow resulting in a high transport rate of H₂S. As long as the pressure difference is not that high that complete mass transfer limitation of SO₂ from the bulk of the gas to the membrane interface occurs, the H₂S and SO₂ molar fluxes will be in stoichiometric ratio and therefore the transport rate of SO₂ is also high. For the same reason the transport rates of H₂S and SO₂ will be high in case of the highest pressure on the SO₂ side and a minimum will exist at a moderate pressure difference over the membrane.

It seems attractive to use a fixed pressure difference over the membrane as the molar fluxes increase substantially, as can be seen in Fig. 5, resulting in smaller membrane area required. A problem in this case is however the transport of inert gas through the membrane which results in the necessity of a bleed stream which will be contaminated with one of the reactants. Therefore it is questionable to conclude that a pressure difference over the membrane in order to reduce the membrane area required would be attractive.

In Fig. 6 the molar flux of elemental sulfur out of the membrane at the H₂S side membrane interface is presented as a function of the pressure difference over the membrane.

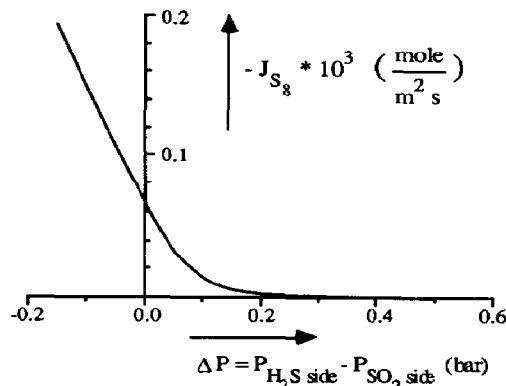


Fig. 6: Molar flux of S₈ out of the membrane at the H₂S side as a function of the pressure difference over the membrane

Although it is possible to transport the elemental sulfur preferentially to one side of the membrane, the pressure difference required is quite high, which may result in large amounts of inerts transported through the membrane with the problem described above.

EXPERIMENTAL VERIFICATION

Conversions of H_2S and SO_2 have been measured at a temperature of 276°C and a pressure of 1.5 bar in absence of a pressure difference over the membrane. The membrane used was obtained from the Netherlands Energy Research Foundation ECN and was made of $\alpha\text{-Al}_2\text{O}_3$ with a mean porediameter of 350 nm, a porosity of 41 % and a thickness of 4.5 mm which was impregnated with $\gamma\text{-Al}_2\text{O}_3$. By varying the ratio of the flow of $\text{H}_2\text{S}/\text{N}_2$ and SO_2/N_2 into the compartments of the membrane reactor, the ratio of the bulk concentrations of H_2S and SO_2 was varied. According to the principle of this reactor, this should result in a shift of the reaction plane in the membrane as the ratio between the driving forces for diffusion of the reactants is varied.

Although the Claus reaction generally cannot be considered irreversible at 276°C , the molar fluxes calculated using this assumption do not deviate substantially from the results taking reversibility into account as was shown by the numerical work studying the influence of reversibility. From the calculations it was also shown that very small pressure differences over the membrane that may occur in the experiments (less than 10 mm H_2O in practice) can be neglected completely. Therefore for the interpretation of this particular system an instantaneous, irreversible reaction in the absence of a pressure difference over the membrane can be assumed, for which the molar flux of H_2S is predicted by equation (25).

$$J_{\text{H}_2\text{S}} = \frac{2 D_{\text{SO}_2 \text{ eff}} c_{\text{SO}_2} + D_{\text{H}_2\text{S} \text{ eff}} c_{\text{H}_2\text{S}}}{L + \frac{D_{\text{H}_2\text{S} \text{ eff}}}{D_{\text{H}_2\text{S}}} \delta_1 + \frac{D_{\text{SO}_2 \text{ eff}}}{D_{\text{SO}_2}} \delta_2} \quad (25)$$

with δ_1 and δ_2 the thickness of the stagnant gas film at the membrane interfaces and $c_{\text{H}_2\text{S}}$ and c_{SO_2} the concentrations in the bulk of the gas

Because the aim of the present experimental investigation is to demonstrate the fundamental working of this membrane reactor and not to obtain exact values of the effective diffusion coefficients, mass transfer resistances in the gas phase, represented in equation (25) by the denominator, were neglected for convenience of interpretation although their total contribution is estimated to be between 25 and 30 % of the total resistance. The denominator in equation (25) is therefore set equal to L and dividing by the bulk concentration of H_2S then results in equation (26).

$$\frac{J_{\text{H}_2\text{S}}}{c_{\text{H}_2\text{S}}} = \frac{D_{\text{H}_2\text{S} \text{ eff}}}{L} + \frac{2 D_{\text{SO}_2 \text{ eff}}}{L} * \frac{c_{\text{SO}_2}}{c_{\text{H}_2\text{S}}} \quad (26)$$

When the molar flux of H_2S , divided by the bulk concentration of H_2S , is plotted as a function of the ratio of the bulk concentrations of SO_2 and H_2S , a straight line results. From the slope and the intercept of this line the effective diffusion coefficients of SO_2 and H_2S can be calculated respectively.

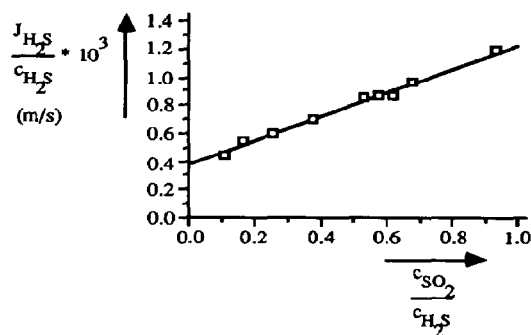


Fig. 7: Conversion measurements at 276°C

In Fig. 7 the molar flux of H_2S divided by the bulk concentration of H_2S is plotted as a function of the ratio of the bulk concentrations of SO_2 and H_2S . To check the results obtained, the molar flux of H_2S divided by the bulk concentration of SO_2 is plotted as a function of the ratio of the bulk concentrations of H_2S and SO_2 . The agreement between the effective diffusion coefficients obtained from these two methods of plotting is within 4 %. The values of the effective diffusion coefficients obtained are:

$$D_{\text{H}_2\text{S} \text{ eff}} = 1.77 * 10^{-6} \text{ m}^2/\text{s}$$

$$D_{\text{SO}_2 \text{ eff}} = 2.13 * 10^{-6} \text{ m}^2/\text{s}$$

From the straight lines obtained combined with reasonable values for the effective diffusion coefficients for H_2S and SO_2 it is concluded that the reaction plane shifts through the membrane depending on the driving forces for diffusion of H_2S and SO_2 as foreseen by the theory.

CONCLUSIONS

A new type of membrane reactor with separated feeding of reactants is presented for processes normally requiring strict stoichiometric feed rates of premixed reactants. The features of this membrane reactor are shown by means of mathematical modelling of molecular diffusion and viscous flow of gases in the membrane, combined with an instantaneous, reversible reaction inside the membrane. It is concluded that mass transfer resistances in the gas phase may be important especially when a pressure difference over the membrane is present. It is demonstrated that a moderate pressure difference over the membrane does not affect the fundamental working of this reactor.

As a model reaction the Claus reaction was selected and by conversion measurements the principle of a reaction plane inside the membrane, shifting as a function of the driving forces of the reactants, is demonstrated.

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NOTATION

B_o	membrane specific parameter	(m^2)
c	concentration	(mole/ m^3)
D_i	diffusion coefficient of component i	(m^2/s)
$D_{i,K}$	Knudsen diffusion coefficient	(m^2/s)
d_p	mean pore diameter	(m)
E_{ij}	equation number i on grid point number j	
h	distance between two grid points	(m)
J_i	molar flux of component i	(mole/ m^2s)
K_{ev}	equilibrium constant	
k_g	mass transfer parameter in the gas phase (D_i / δ)	(m / s)
L	membrane thickness	(m)
nc	number of components	(-)
P	pressure	(Pa)
R	gas constant	(J/mole K)
R_i	reaction rate of component i	(mole/ m^3s)
T	temperature	(K)
v_i	variable number i	
x	coordinate perpendicular to the membrane	(m)
x_i	molar fraction of component i	(-)
δ	thickness of the stagnant gas film	(m)
ϵ	porosity of the membrane	(-)
η	viscosity of the gas	(Pa s)
ν	stoichiometric coefficient	(-)
τ	tortuosity of the membrane	(-)

indices

A	component
B	component
bulk	bulk of the gas
C	component
D	component
diff	diffusive
eff	effective
int	membrane interface
k	number of grid point
visc	viscous

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